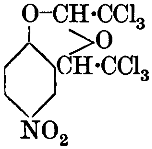
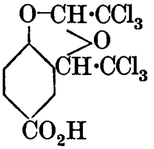
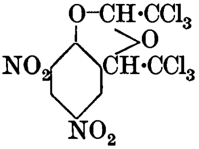
CCLXV.—*The Condensation of Chloral with Phenol.*

By Frederick Daniel Chattaway and Alexander Allan Morris.

It has been shown recently (J., 1926, 2720; this vol., p. 685) that in presence of concentrated sulphuric acid, chloral reacts readily with *p*-nitrophenol and with *p*-hydroxybenzoic acid, yielding respectively anhydro-5-nitro- (I) and anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (II)


(I.)

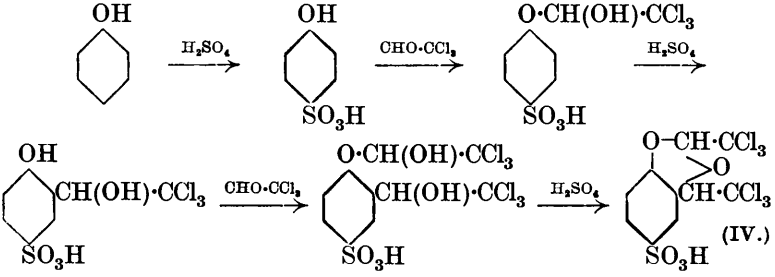

(II.)


(III.)

Chloral appears to condense in this way only with phenols in which the hydrogen in the para-position to the hydroxyl has been replaced by other groups.

When phenol itself is added to chloral suspended in concentrated sulphuric acid, an immediate reaction occurs, and an oily liquid separates which rapidly changes into an opaque, white solid. This readily dissolves in alcohol, giving a colourless solution from which nothing crystallises on cooling. On evaporating off the solvent, a viscid liquid is left which solidifies to a colourless, transparent, resin-like mass, the constitution of which has not yet been determined.

If, however, the phenol is first dissolved in the sulphuric acid, whereby *p*-phenolsulphonic acid is formed, this on addition of chloral slowly reacts, forming a compound (IV) analogous in structure to the above (I and II).

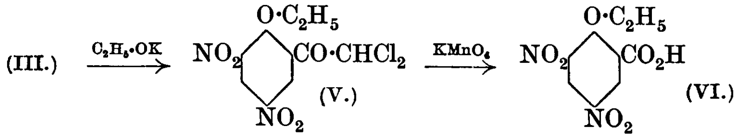

(IV.)

This compound behaves in all respects as a normal sulphonic acid. It is a colourless solid with no definite melting point. It crystallises with three molecules of water, two of which can be removed by heating, and forms well-crystallised salts. When acted upon by phosphorus pentachloride, it forms a *sulphonyl chloride.* This with ethyl and methyl alcohol yields *esters,* with ammonia a *sulphonamide,* and with aniline a *sulphonanilide.*

Its constitution is similar to that of the condensation product (I) yielded by *p*-nitrophenol, since both compounds on nitration yield *anhydro*-3 : 5-*dinitro*-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene* (III).

The molecules of water are probably attached to the sulphonic residue, the anhydride ring remaining unbroken, since, although only two are removed by heating, yet the ammonium salt is obtained in the anhydrous condition.

The constitution of the acid is further confirmed by the product of the action of alcoholic potash on the dinitro-derivative (III), whereby ωω-*dichloro*-3 : 5-*dinitro*-2-*ethoxyacetophenone* (V) is formed, which on oxidation by potassium permanganate yields 3 : 5-dinitro-2-ethoxybenzoic acid (VI).



EXPERIMENTAL.

Anhydro-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphonic Acid* (IV).—Phenol (100 g.; 1 mol.) was added slowly to 1000 c.c. of well-cooled sulphuric acid (*d* 1·8). After an hour, 400 g. of chloral hydrate (2 mols. + 50 g. excess) were gradually added with constant stirring. The mixture was then kept at the ordinary temperature for 4 days with occasional vigorous shaking. Reaction slowly took place, a bulky, white solid separating in the body of the solution, whilst a solid crust of metachloral formed on the surface. The solid products were filtered off on asbestos, and extracted with boiling water until the filtrate no longer deposited crystals when cooled and strongly acidified. The *sulphonic acid* was thus separated from the metachloral, which was left as a white solid insoluble in boiling water. The filtered aqueous extracts were mixed and evaporated until oily streaks appeared on the surface of the boiling liquid. On cooling, the sulphonic acid separated in viscid oily drops which crystallised into a mass of very thin, lustrous plates (yield, 150 g.). The sulphonic acid is moderately easily soluble in boiling benzene and separates from this solution in very thin, colourless, lustrous, irregular plates containing three molecules of water (Found: C, 23·75; H, 2·3; Cl, 42·2. $C_{10}H_6O_5Cl_6S,3H_2O$ requires C, 23·8; H, 2·4; Cl, 42·1%).

When heated, the trihydrated acid partly liquefies between 125° and 130°, small prismatic crystals of a monohydrated acid separating.

When heated for ½ hour at 110°, the acid loses two molecules of water, leaving a crystalline aggregate of small, colourless, prismatic crystals of the monohydrated acid (Found: Loss of water at 110°, 7·0. $C_{10}H_6O_5Cl_6S,3H_2O \longrightarrow H_2O$ requires loss of water, 7·1%).

The monohydrated acid is very easily soluble in alcohol and acetone, and very sparingly soluble in boiling benzene and chloroform. It can be recrystallised by dissolving it in boiling acetic acid and adding concentrated hydrochloric acid a little at a time until the solution shows a slight turbidity. On cooling, the acid separates in small, colourless prisms which melt with decomposition between 150° and 166° (Found: C, 25·5; H, 1·7; Cl, 45·3; S, 7·0. $C_{10}H_6O_5Cl_6S,H_2O$ requires C, 25·6; H, 1·7; Cl, 45·4; S, 6·85%).

When moistened with a little cold water, the crystals of the monohydrated acid swell up into an amorphous sticky mass, which on warming gives a clear solution from which the hydrated acid crystallises on addition of a little concentrated hydrochloric acid.

It forms an anhydrous *ammonium* salt which crystallises from a dilute aqueous solution of ammonia in very small, colourless prisms (Found: C, 25·9; H, 2·0; Cl, 45·5. $C_{10}H_9O_5NCl_6S$ requires C, 25·65; H, 1·9; Cl, 45·5%).

Nitration of Anhydro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene-5-sulphonic Acid.—The sulphonic acid (40 g.) was added to a mixture of 150 c.c. of nitric acid (*d* 1·5) and 5 c.c. of concentrated sulphuric acid and heated to boiling. After cooling, the brown solution was poured on crushed ice; the dinitro-compound (III) then separated as a greenish-white solid, which, after drying, was recrystallised from boiling alcohol.

A product similar in every way was obtained when anhydro-5-nitro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene was nitrated in the same manner.

Anhydro-3 : 5-dinitro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (III) is easily soluble in boiling acetic acid, alcohol, acetone, and benzene, and crystallises from all these solvents in two polymorphic modifications. On cooling, a solution of the compound in about three times its weight of boiling alcohol the labile modification first separates as slender, silky needles. On allowing these to stand in the mother-liquor, pale yellow rhombohedra of the stable form appear and grow at the expense of the labile form, which dissolves and finally disappears. Both forms melt at 163° (Found: N, 6·0; Cl, 46·1. $C_{10}H_4O_6N_2Cl_6$ requires N, 6·1; Cl, 46·2%).

The position of the second nitro-group in this compound was established by its behaviour with alcoholic potash. The finely powdered dinitro-compound (25 g.) was gradually added to a solution of 30 g. of potassium hydroxide in 400 c.c. of alcohol, well cooled in a freezing mixture; it dissolved, giving a deep red solution, and chloroform was produced. After about 15 minutes, the liquid was neutralised by hydrochloric acid and the alcohol distilled off in a current of steam; *ωω-dichloro-3 : 5-dinitro-2-ethoxyacetophenone* (V) then separated as a liquid, which on cooling solidified to a crystalline, yellow mass (17·5 g.). It is readily soluble in boiling alcohol, from which it separates in small, yellow prisms, m. p. 82—84°, which darken when exposed to strong sunlight (Found: N, 8·7; Cl, 22·2. $C_{10}H_8O_6N_2Cl_2$ requires N, 8·7; Cl, 22·0%).

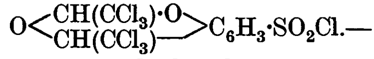
It yields an *osazone*,

$$OEt\cdot C_6H_2(NO_2)_2\cdot C(:N\cdot NH\cdot C_6H_3Cl_2)\cdot CH:N\cdot NH\cdot C_6H_3Cl_2,$$

when heated with an alcoholic solution of 3 : 5-dichlorophenylhydrazine. This compound is very sparingly soluble in boiling chloroform, from which it separates in minute, orange needles, m. p. 224° (Found: N, 14·4; Cl, 24·6. $C_{22}H_{16}O_5N_6Cl_4$ requires N, 14·3; Cl, 24·2%).

Oxidation of ωω-Dichloro-3 : 5-dinitro-2-ethoxyacetophenone by Permanganate.—ωω-Dichloro-3 : 5-dinitro-2-ethoxyacetophenone (15 g.) was added to a hot aqueous solution of 15 g. of potassium permanganate, and boiled until the oily drops first formed on the addition of the compound disappeared. The deep yellow filtrate from the precipitated manganese dioxide was concentrated, and an excess of hydrochloric acid added; 3 : 5-dinitro-2-ethoxybenzoic acid then separated, m. p. 132·5° (compare Ullmann, *Annalen*, 1909, **336**, 85) (Found: C, 42·6; H, 3·3; N, 10·9. Calc. for $C_9H_8O_7N_2$: C, 42·2; H, 3·1; N, 10·9%).

Anhydro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene-5-sulphonyl Chloride,



$$O<\begin{matrix}CH(CCl_3)\cdot O\\ CH(CCl_3)—\end{matrix}>C_6H_3\cdot SO_2Cl.$$—

The monohydrated acid (30 g.) and powdered phosphorus pentachloride (55 g.) were heated on the water-bath for 5 minutes, and the viscous pale brown oil formed was poured slowly over crushed ice. The *sulphonyl chloride* separated as a white solid, and crystallised from ether–light petroleum in very slender, colourless needles, m. p. 130·5° (Found: C, 25·5; H, 1·3; Cl, 52·6. $C_{10}H_5O_4Cl_7S$ requires C, 25·6; H, 1·1; Cl, 52·9%).

When boiled with any alcohol it reacts readily and yields the corresponding alkyl sulphonate. The *methyl* ester separates from boiling methyl alcohol, in which it is moderately easily soluble, in small, highly refracting, colourless prisms, m. p. 150° (Found: C, 28·3; H, 1·7; Cl, 45·7. $C_{11}H_8O_5Cl_6S$ requires C, 28·4; H, 1·7; Cl, 45·8%). The *ethyl* ester separates from boiling ethyl alcohol in small, colourless, elongated, irregular plates, m. p. 143° (Found: C, 29·4; H, 2·2; Cl, 44·5. $C_{12}H_{10}O_5Cl_6S$ requires C, 30·1; H, 2·1; Cl, 44·4%).

The sulphonyl chloride also reacts readily with ammonia and with aniline in boiling alcohol to form a sulphonamide and a sulphonanilide.

Anhydro-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphonamide* separates from boiling alcohol, in which it is readily soluble, in colourless, small, silvery plates, m. p. 207° (Found: N, 3·2; Cl, 47·3. $C_{10}H_7O_4NCl_6S$ requires N, 3·1; Cl, 47·3%).

When dissolved in acetic acid and chlorinated, it yields *anhydro*-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphondichloroamide*, which dissolves easily in chloroform and separates in colourless, slender prisms, m. p. 165—174° (decomp.) (Found: Cl as $\cdot NCl_2$, 13·4. $C_{10}H_5O_4NCl_8S$ requires Cl as NCl_2, 13·7%).

Anhydro-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphonanilide* crystallises from dilute alcohol in very slender, silky, hair-like prisms, m. p. 168·5° (Found: N, 2·7; Cl, 40·5. $C_{16}H_{11}O_4NCl_6S$ requires N, 2·7; Cl, 40·5).

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